

FINAL TECHNICAL REPORT

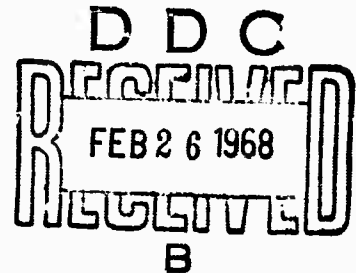
ELECTRON DIFFRACTION STUDIES AT ELEVATED TEMPERATURES

December 1967

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**for selected
periods**

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The post-doctorates research associates and graduate students who contributed to the over-all electron diffraction research program have also been supported in part by Cornell University, N.S.F. (GP-4291) and the Material Science Center, ARPA-SD-68.

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GENERAL OBJECTIVES OF OUR ELECTRON DIFFRACTION PROGRAM

The following brief outline of our electron diffraction research efforts will serve as a framework for that portion which is supported by the Office of Naval Research. Our studies may be catalogued under five headings; of these ONR has supported specifically Items 1-4, and it is evident that as a consequence of this support our overall effort has been considerably enhanced.

- (1) Development of techniques: This includes (a) the "checking-out" and improvement in the operation of our new electron diffraction apparatus, both in the "convergent incidence" and "parallel incidence" modes; (b) the construction and testing of elevated temperature sample holders and nozzles; (c) extension of our computer programs (currently in process of changing from CDC 1604 to an IBM 360/65; and (d) the conversion of our microdensitometer to digitized operation so as to achieve increased precision in the measurement of photographic density at specified diffraction ring radii.
- (2) The calibration of sectors and measurement of atom form factors are closely coupled. To date, all electron diffractionists were forced to accept calculated atom form factors for Ar or He to calibrate their sectors. We are in process of testing an experimental procedure in which these two functions can be obtained separately. It is based on precise measurement of the scattering by species with the same formula weight but different molecular weights, such as C_2H_2 , C_4H_4 and C_6H_6 , the geometric structures of which are known with considerable accuracy. For this set of experiments, the parallel mode of operation is particularly favorable since it permits us to obtain scattering data at low angles of diffraction.
- (3) Determination of the structures of selected compounds for which no structural data are available. These studies favor species which are obtainable at elevated temperatures (MX_4), and of radicals (for example NF_2 and SO_3F).
- (4) Determination of the structures of species which can be prepared only with the admixture of co-products, the structures of which are known. In these cases our

minimal acceptable standard for precision will have to be relaxed (for example, KrF_2 in the presence of SiF_4 ; $\text{H}_3\text{B}_3\text{O}_3$ in the presence of H_2).

(5) Determination of the structures of strained ring hydrocarbons, and rationalization of these results in terms of empirical expressions currently used for estimating energies of specific conformations.

PUBLICATIONS

An Electron Diffraction Study of the Structure of NF_2 and N_2F_4 , R. K. Bohn and S. H. Bauer, *Inorg. Chem.* **6**, 304 (1967).

An Electron Diffraction Study of the Structures of cis and trans Difluorodiazine, R. K. Bohn and S. H. Bauer, *Inorg. Chem.* **6**, 309 (1967).

The Molecular Structure of Perfluorodiazirine, J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 5527 (1967).

The Structures of C_6 , B_3N_3 and C_3N_3 Ring Compounds, S. H. Bauer, K. Katada and K. Kimura, L. Pauling's 65th Anniversary Festschrift, Freeman and Co., (1967), pp. 681-697.

An Electron Diffraction Study of KrF_2 and Comments on the Structure of XeF_6 , W. Harshbarger, R. K. Bohn and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 6466 (1967).

The Molecular Structure of Trimethylenecyclopropane, E. A. Dorko, J. L. Hencher and S. H. Bauer, *Tetrahedron*, **24**, (1968).

Revision of Structure of SOF_4 , J. L. Hencher, D. W. J. Cruickshank and S. H. Bauer, *J. Chem. Phys.*,

PAPERS SUBMITTED FOR PUBLICATION (or in final stages of preparation)

Structures and Conformations of the Cyclohexadienes, H. Oberhammer and S. H. Bauer, submitted to the *J. Chem. Phys.*

The Structures of Norbornane and 1,4-Dichloronorbornane, J. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, submitted to the *J. Am. Chem. Soc.*

The Structure Tricyclo[3, 3, 0, 0^{2, 6}]octane as Determined by Electron Diffraction, J. F. Chiang and S. H. Bauer, submitted to *Trans. Farad. Soc.*

The Structure of 4-Chloronortricyclene as Determined by Electron Diffraction, J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, will be submitted to *Tetrahedron*.

The Structures of Borazine and B-aminoborazine. W. Harshbarger, G. Lee, R. F. Porter and S. H. Bauer, will be submitted to Inorg. Chem.

Re-investigation of the Structure of N_2F_4 , Mark Cardillo and S. H. Bauer, will be submitted to Inorg. Chem.

The Structures of Boroxine and of $N_4(CH_3)_2BH$. C. H. Chang, R. F. Porter and S. H. Bauer, will be submitted to J. Am. Chem. Soc.,

Construction and Performance of a Parallel Incidence Electron Diffraction Apparatus, S. H. Bauer, J. L. Hencher and H. Oberhammer, will be submitted to Rev. Sci. Inst.

Modifications of a Jarrell-Ash Microdensitometer for Rotation of Plates and Digitized Scanning. S. H. Bauer and R. Jenkins, will be submitted to Rev. Sci. Inst.

Abstracts and tabular summaries of the above papers are attached to this report.

COLLABORATION WITH FORMER COWORKERS

At this time two of our former postdoctorate associates and one former graduate student have University appointments and are continuing with molecular structure investigations. Since they do not have electron diffraction units available in their laboratories we have arranged for them to analyze plates taken in our laboratory. Many of these compounds fit within the NSF sponsored program; however, the following are of interest to ONR:

Dr. J. L. Hencher and his students (University of Windsor, Windsor, Ontario, Canada).



Dr. J. Martinez (John Fisher College, Rochester, New York).



CONSTRUCTION AND PERFORMANCE OF A PARALLEL INCIDENCE ELECTRON DIFFRACTION APPARATUS

S. H. Bauer, J. L. Hencher and H. Oberhammer

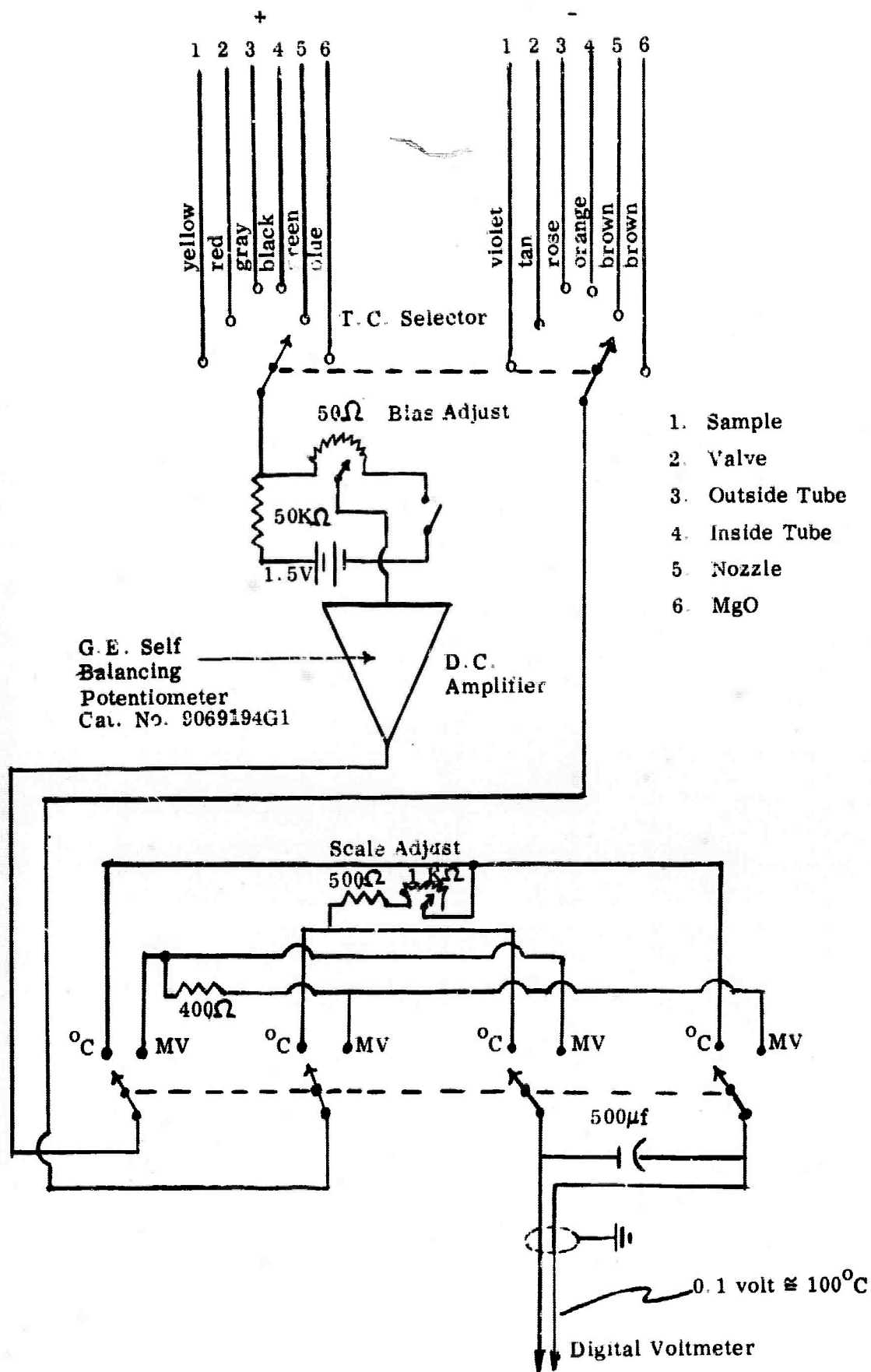
[To be submitted to Rev. Sci. Inst.]

ABSTRACT

An electron diffraction apparatus for gaseous samples was constructed, which provided the option of irradiating the sample either with a convergent ray focused onto the recording plate (as is conventional), or with a parallel ray which is focused onto the plate by two large aperture lenses after the ray had intersected the gas jet. When the projection lens currents are properly adjusted, the diffraction pattern is focused at a focal plane (rather than a sphere), and the radii of the diffraction rings are determined by the lens parameters, independent of sample location or spread. The parallel incidence mode of operation has features which are particularly advantageous for the study of samples which are available at low densities only, and for the recording of diffraction intensities at low scattering angles.

In the design of this electron diffraction unit particular attention was given to the following aspects: (i) rigidity of construction and clean operation were obtained through the use of heavy stainless steel walls which were hydrogen brazed at the vacuum joints; (ii) low background pressures are maintained during sample injections by means of two 4" diffusion pumps with freon cooled traps, and two cryosorption panels; (iii) highly regulated voltage and lens current supplies are fully monitored with high precision meters; (iv) complete circular patterns are recorded on 4 x 5" plates to permit averaging of the density patterns over 360° plate rotations; ten plates can be exposed per run.

Focus conditions, resolution and contrast have met initial design specifications in all respects but one, the fourth lens is not strong enough to permit parallel incidence operation above 57 kv. For the convergent incidence mode voltages up to 75 kv are regularly employed. The full range in q which can be covered is 1 to 130 \AA^{-1} . No significant ring ellipticity has been observed. Several sample holders and nozzles for ambient and elevated temperatures have been constructed.



MULTIPLE STATION READ-OUT: Thermocouples to meter

MODIFICATIONS OF A JARRELL-ASH MICRODENSITOMETER
FOR ROTATION OF PLATES AND DIGITIZED SCANNING

S. H. Bauer and R. Jenkins

[To be submitted to Rev. Sci. Inst.]

ABSTRACT

A Jarrell-Asch microdensitometer (Model No. 23-100) was modified in a number of respects to provide flexibility of operation and optimum precision in recording densities at specified plate positions. It is used for reducing electron diffraction patterns recorded on 4" x 5" plates. (a) A special carriage was mounted on the sample stage; this can be rotated at about 600 rpm around the center of diffraction, as the density is scanned along a diameter. The plate emulsion remains within 0.030" of the light collecting prism. (b) A high precision transparent scale with markings was inserted in the comparison stage; its image actuates a photosensor as the scale travels. The signals, which correspond to 250 μ of plate motion, are recorded as pips along the recorder paper margin. (c) Matched RC networks were inserted in the phototube amplifier circuits to provide a selection of response times (minimal, 3/4, 2, and 4 sec) to match selected plate scan rates. (d) High precision data are collected in digitized form.

For digitized operation the plate carriage is driven by a precision screw coupled to a shaft encoder. The logic sequence consists of the following steps: advance a present number of microns; stop for 0.2 to 5 sec (optional); light intensity which measures plate transmission is then read and digitized; print the number of microns advanced and the phototube output voltage; advance, etc. After ten such steps the reference voltage is sampled and printed without further plate position increment, and then the cycle is restarted. Various manual options are also available.

PRECISION SCREW DRIVE FOR PLATE CARRIAGE

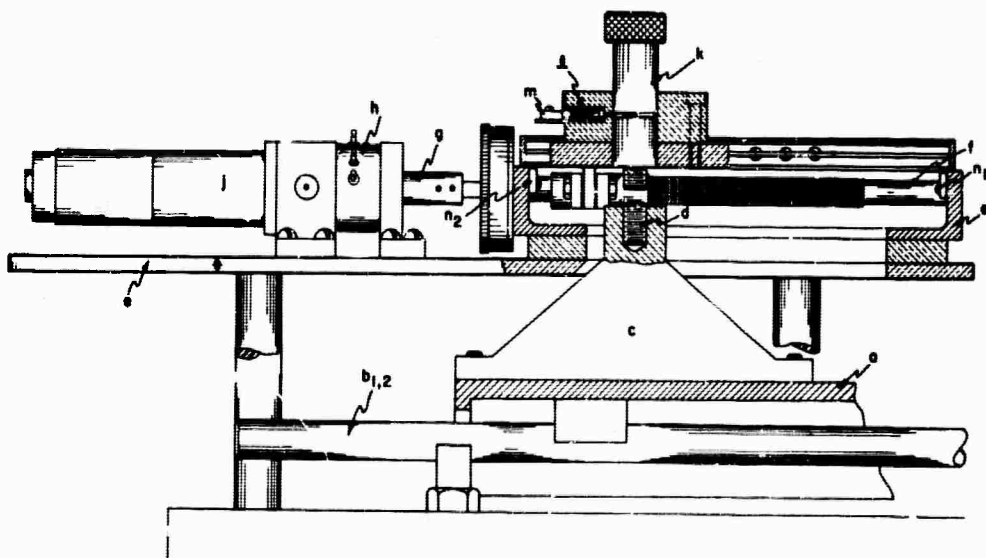
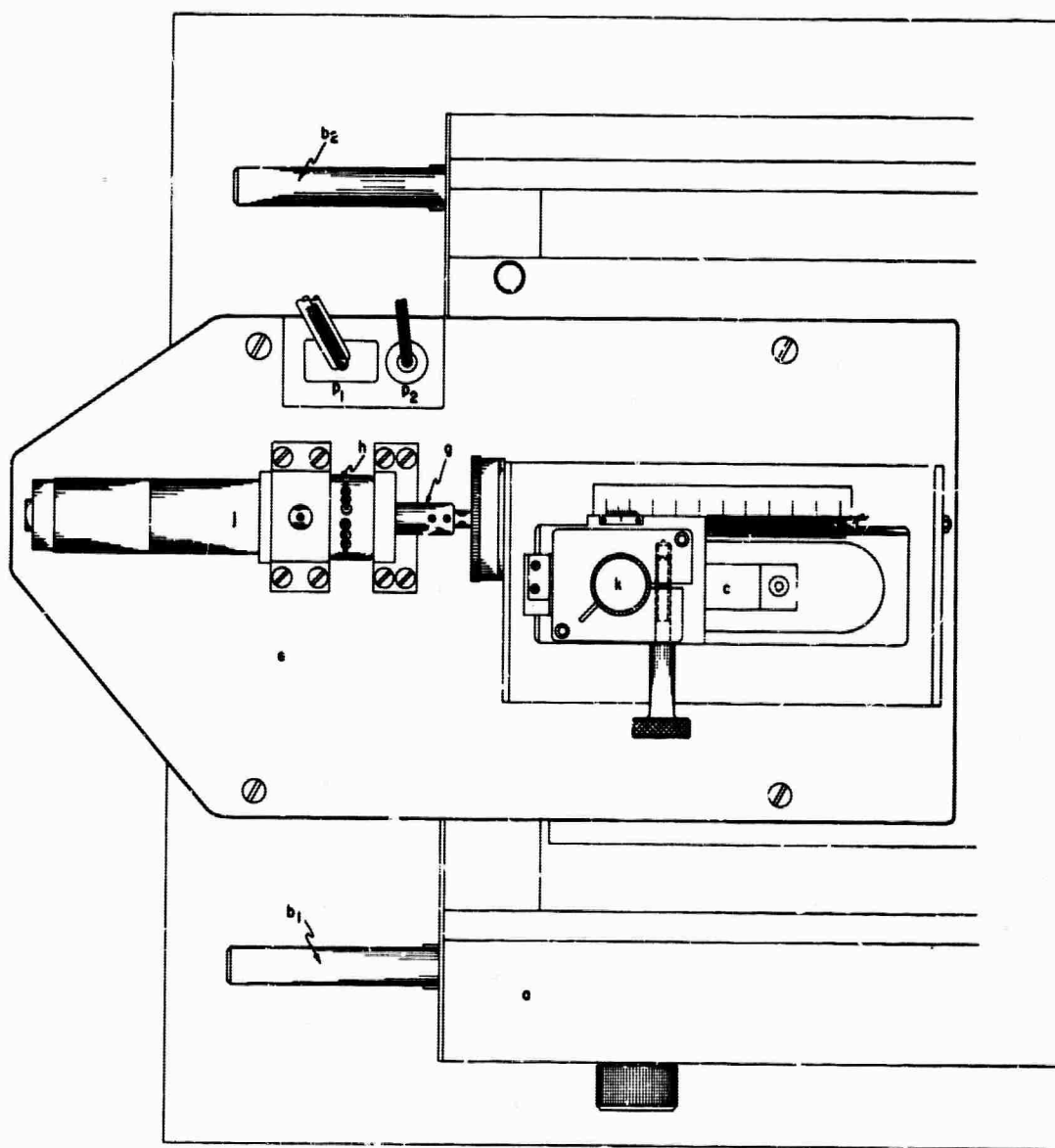
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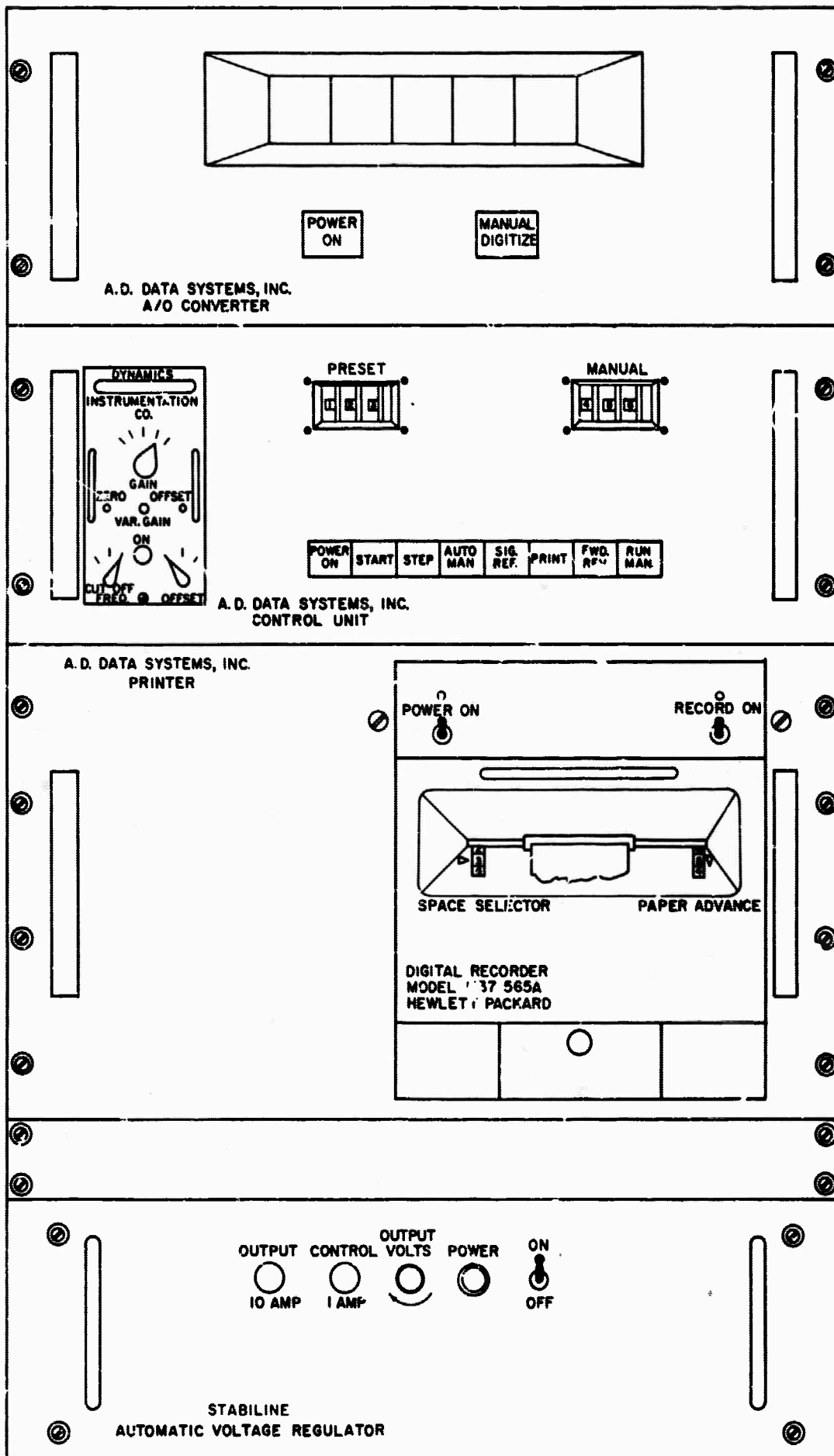
- a-massive carriage upon which rotating plate stage is fixed
- b_{1,2}-precision ground rail bars upon which carriage slides
- c-heavy dual triangular block attached to carriage, tapped to receive coupling screw (k) at d.
- e-dural mounting plate for supporting drive screw, motor, shaft encoder, etc.
- f-precision screw, 10 cm long, pitch 1mm/turn
- g-couple - screw shaft to encoder (k) shaft
- h-shaft encoder, 1000 units per revolution
- j-drive motor, controlled by preset pulse number from encoder
- k-steel coupling screw, which attaches travel nut and plate to the block c.
- l-spring loaded rod - to activate limit switch m such that circuit for original motor drive for carriage remains open unless k is in up position
- m-limit switch in series with electrical clutch for J-A motor to carriage
- n₁, n₂-limit switches in series with motor j
- p₁-multiplug connections - shaft encoder and motor to control unit
- p₂-connections to limit switches

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REINVESTIGATION OF THE STRUCTURE OF N_2F_4

M. Cardillo and S. H. Bauer

[Will be submitted for publication in Inorganic Chemistry]

ABSTRACT

The structure of N_2F_4 has been investigated in the gaseous, liquid and solid phases by a variety of spectroscopic and diffraction techniques. Recent NMR data for the liquid indicated that both the trans and gauche conformations were present in approximately equal molar proportions at about $-150^{\circ}C$. The initial infrared and raman data were interpreted in terms of the gauche conformation only; however, subsequent detailed analyses showed that both isomers were present, again in roughly equal proportions. A microwave study of the gas phase showed the presence of the gauche form. Since the trans form does not have a dipole moment no conclusion as to its absence or presence could be based on the microwave results.

The first electron diffraction results on N_2F_4 obtained in this laboratory (Bohn and Bauer, Inorg. Chem., 6, 304, (1967)) were based on photographs taken with our old apparatus and were interpreted on the basis of gauche form only. These data were somewhat limited in angular range, and doubt arose subsequently as to the purity of the sample. In view of the current spectroscopic evidence, a new sample was obtained for which an accurate analysis was available. It showed N_2F_4 at 97.1% with the remaining impurities as N_2O , CO_2 , N_2F_2 , NF_3 and NO . The stainless steel cylinder and valve in which the sample was shipped from the Rohm and Haas Gorgas Labs (Huntsville) was attached directly to the stainless steel inlet tube and nozzle, in the electron diffraction apparatus. The lead tube and nozzle were conditioned thoroughly by flowing excess N_2F_4 through them. Diffraction data was obtained over the range $5 < q < 130$, and analyzed according to standard procedures. It soon became evident that the new diffraction data could not be interpreted on the assumption that only the gauche isomer was present, a significant fraction of the material is in the trans form. At the

current stage of analysis of the data a good account of the diffraction pattern can be made by assuming equal amounts of the gauche and trans forms, with the following interatomic distances

	<u>Cardillo</u>	<u>Bohn</u>
N-N	1.50 Å ⁰	1.53 Å ⁰
N-F	1.375 Å ⁰	1.393 Å ⁰
∠FNF	103.7°	103.7°
∠NNF	g { 100° 103.5°	{ 99.0° 103.5°
	t 101°	
twist ∠	g 69.3°	69.3

The analysis is being continued. The new plates are being remeasured with the digitized microphotometer to provide more precise diffraction data.

THE STRUCTURES OF BORAZINE AND B-MONOAMINOBORAZINE

W. Harshbarger, G. Lee, R. F. Porter and S. H. Bauer

[To be submitted for publication in Inorganic Chemistry]

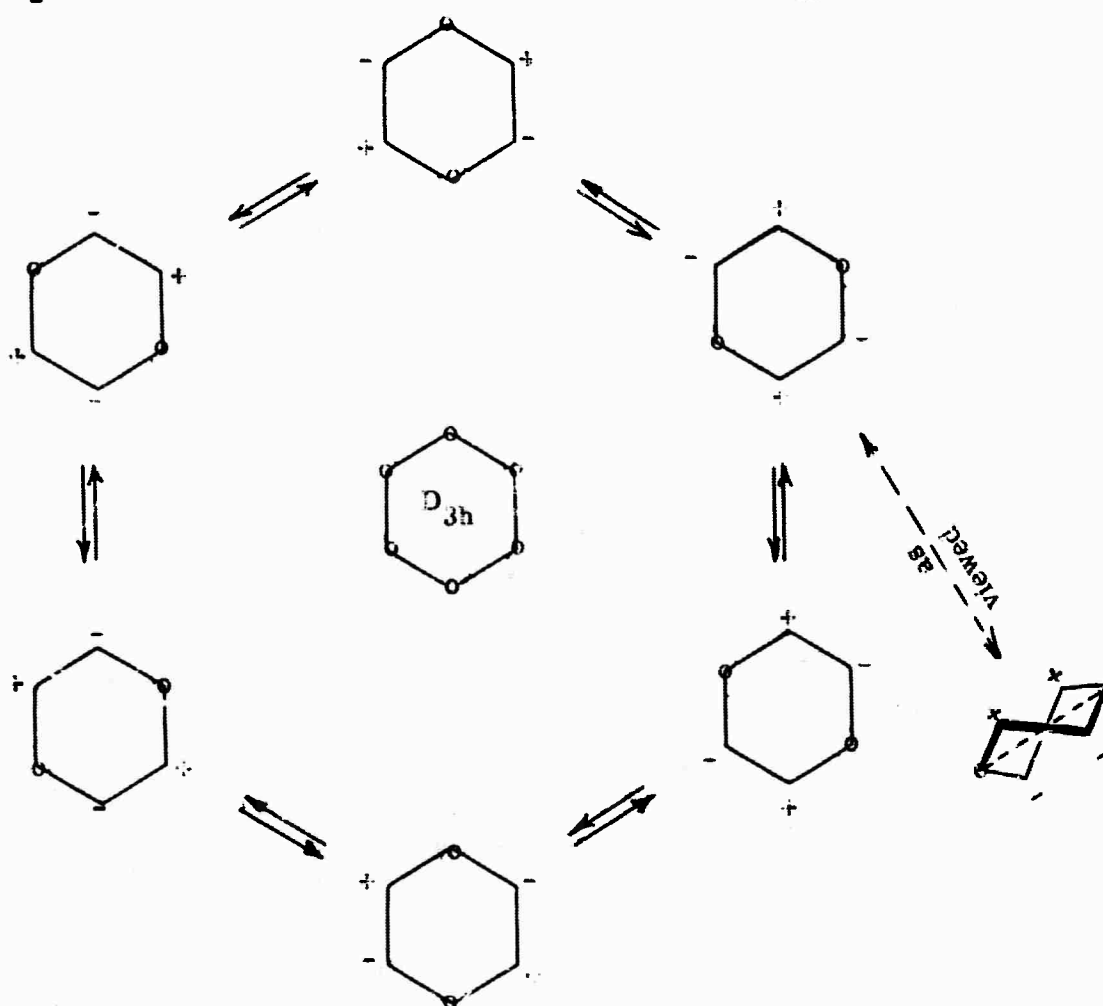
ABSTRACT

The gas phase molecular structures of borazine and B-aminoborazine were investigated by electron diffraction. For $B_3N_3H_6$ two sets of sectorized photographs were taken of separately prepared and highly purified samples. The diffraction data, which agreed well with each other, covered the range $8 < q < 125 \text{ \AA}^{-1}$. After several stages of refinement the radial distribution curve was resolved into pairwise scattering contributions for a benzene-like structure, with D_{3h} symmetry. However, least squares analysis of the molecular intensity curve gave somewhat lower standard deviations for non-planar C_{3v} and C_2 models. The D_{3h} model is best fitted by the following parameters: $(B-N) = 1.435 \pm 0.001 \text{ \AA}$; $(B-H) = 1.244 \pm 0.006 \text{ \AA}$; $(N-H) = 1.034 \pm 0.006 \text{ \AA}$ and $\angle BNB = 117.0^\circ \pm 0.2^\circ$; the C_{3v} structure must be rejected because borazine has no permanent dipole moment. While the electron diffraction data favor a non-planar time average structure, the best mode of description is not yet clear. Perhaps other data can be utilized to determine which non-planar model best describes the molecular structure of borazine.

In a preliminary analysis of B-aminoborazine patterns, the B_3N_3 ring was assumed to have D_{3h} symmetry, and the $B-NH_2$ bond to lie along the ring bisector. The deduced bond lengths are $(B-N)_{\text{ring}} = 1.431 \pm 0.005 \text{ \AA}$; $(B-N)_{\text{amino}} = 1.448 \pm 0.030 \text{ \AA}$. $(B-H) = 1.154 \pm 0.024 \text{ \AA}$; $(N-H)_{\text{ring}} = 0.985 \pm 0.017 \text{ \AA}$; $(N-H)_{\text{amino}} = 1.016 \pm 0.028 \text{ \AA}$.

CORRELATION OF C_2 WITH D_{3h}

The E'' normal vibrational mode of D_{3h} which generates C_2 conformations are illustrated below. If the planar structure is not at the minimum potential, the six equivalent C_2 structures can interconvert without passing through D_{3h} , as indicated.



The two lowest fundamental frequencies of borazine (288 cm^{-1} and 394 cm^{-1}) have been assigned to E'' and A_2'' , respectively, corresponding to 404 cm^{-1} (ν_{20} , E_{2u}) and 530 cm^{-1} (ν_8 , B_{2g}) of benzene.

INTERATOMIC DISTANCES IN BORAZINE (in Å⁰)

	Planar, D _{3h}		Non-Planar, C ₂	
	1st Set	2nd Set	1st Set	2nd Set
N-H	1.0386 ± .0033	1.0306 ± .0044	1.0470 ± .0031	1.0403 ± .0040
B-H	1.2486 ± .0049	1.2386 ± .0051	1.2648 ± .0047	1.2589 ± .0051
B-N	1.4349 ± .0004	1.4346 ± .0004	1.4358 ± .0004	1.4360 ± .0004
∠NBN	117.20° ± .085°	116.94° ± .078°	117.3° ; 117.7°	117.0° ; 117.3°
N...N	2.4495	2.4455	2.4569 ± .0026	2.4538 ± .0023
	2.5196	2.5523	2.5094 ± .0034	2.5105 ± .0030
			2.5060	2.5059
B...N	2.8689	2.8682	2.8674	2.8662
			2.8588	2.8543
l(NH)	.0679 ± .0029	.0780 ± .0039	.0695 ± .0025	.0793 ± .0030
l(BH)	.0677 ± .0048	.0708 ± .0057	.0646 ± .0040	.0681 ± .0041
l(BN)	.0583 ± .0003	.0578 ± .0004	.0580 ± .0003	.0575 ± .0003
l(N...N)	.0667 ± .0013	.0668 ± .0015	.0697 ± .0013	.0712 ± .0012
l(B...B)	.0667 ± .0013	.0668 ± .0015		
l(B...N)	.0798 ± .0020	.0679 ± .0018	.0803 ± .0017	.0699 ± .0013
χ _E	.0585	.0778	.0397	.0420

Residual errors

THE STRUCTURES OF BOROXINE AND OF $N_4(CH_3)_2BH$

C. H. Chang, R. F. Porter and S. H. Bauer

[Will be submitted for publication in J. Am. Chem. Soc.]

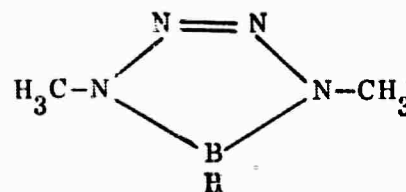
ABSTRACT

Boroxine is a specie which is unstable at room temperature. It can be prepared only in the presence of excess hydrogen, by exploding a mixture of equal molar quantities of diborane and oxygen. The products are solid B_2O_3 and gaseous H_2 and $H_3B_3O_3$. Under these conditions at room temperature the lifetime of $H_3B_3O_3$ is about 20 min. By testing mixtures C_6H_6 and H_2 we established that adequate resolution can be obtained via electron diffraction analysis for a 1/9 mixture. Hence several sets of diffraction photographs of $H_3B_3O_3/H_2$ were obtained and the data were reduced according to the usual procedures.

In the analysis, we assumed that the molecule consisted of a planar 6-member ring of alternating boron and oxygen atoms. On the basis of D_{3h} symmetry, the following interatomic distances were deduced from a least squares analysis of the intensity pattern.

	$r_{ij} (A^0)$	$\sigma_{ij} (A^0)$
B-H	$1.186 \pm .015$	[0.0838]
B-O	$1.377 \pm .003$	$0.0480 \pm .0013$
B...B } {	2.388	$0.0635 \pm .0030$
O...O } {	2.383	
B...O	2.754	$0.0604 \pm .0062$
$\angle BOB$	$120^\circ \pm 0.5^\circ$	

A sample of N-dimethylcyciotetrazino borane was obtained from Dr. J. H. Morris (Kingston College of Technology, England). This unusual five-member ring which consists of 4N atoms and 1B merits careful investigation. The available infrared spectra indicate that the sample we studied has a symmetric structure



The electron diffraction analysis is incomplete, however, it is quite clear that neither the methyl groups nor the boron atom are coplanar with the four nitrogen atoms.

THE STRUCTURE OF 4-CHLORONORTRICYCLENE AS DETERMINED
BY ELECTRON DIFFRACTION

J. F. Chiang, C. F. Wilcox, Jr. and S. H. Bauer

[to be submitted for publication in Tetrahedron]

ABSTRACT

Sectored electron diffraction photographs were taken with the sample at room temperature. The range in scattering angle was $q = 4$ to 98 . Magnesium oxide patterns were recorded to provide a scale factor. Following the usual procedures for photographic density calibration and background refinement, a radial distribution curve was obtained from the reduced molecular intensity function. A model based on C_{3v} symmetry was then readily fitted to the resolved peaks. Theoretical models were characterized by eight structural parameters and five vibrational amplitudes. The remaining amplitudes were set equal to values experimentally reported for similar structures. A least squares program for error minimization relative to the scattered intensity converged to the following structure:

$$\langle C-C \rangle_{3\text{-ring}} = 1.510 \pm 0.003 \overset{O}{\text{\AA}}$$

$$\langle C-C \rangle_{5\text{-rings}} = 1.535 \pm 0.005 \overset{O}{\text{\AA}}$$

$$\langle C-H \rangle_{av} = 1.106 \pm 0.002 \overset{O}{\text{\AA}}$$

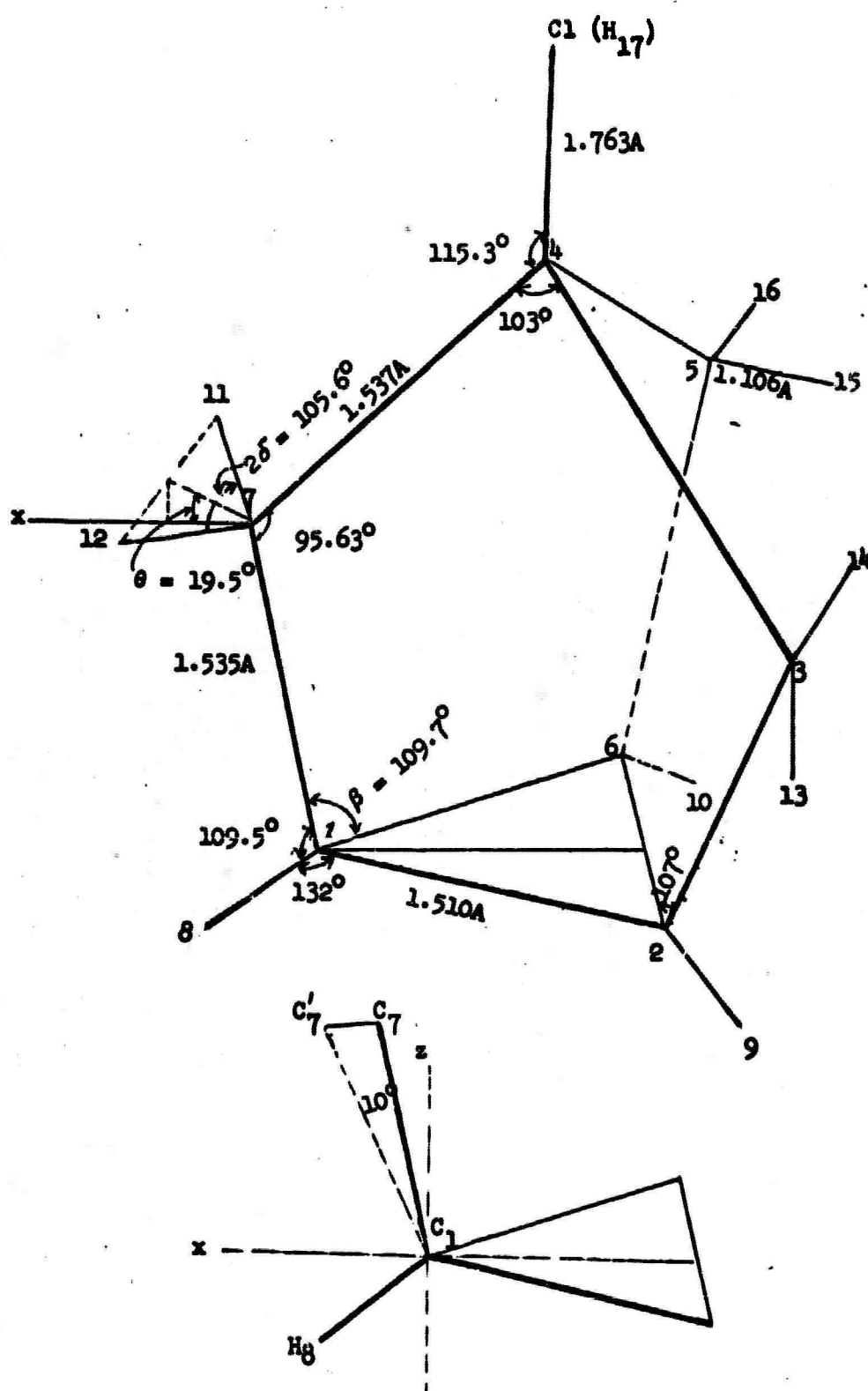
$$\langle C-C \rangle = 1.762 \pm 0.002 \overset{O}{\text{\AA}}$$

These geometric parameters are briefly compared with comparable distances found in the parent hydrocarbon and in related molecules.

GEOMETRIC STRUCTURAL PARAMETERS FOR 4-CHLORONORTRICYCLEN

C_1-C_2	$1.510 \pm 0.008\text{\AA}$
C_2-C_3	$1.535 \pm 0.005\text{\AA}$
C_1-C_7	$1.537 \pm 0.003\text{\AA}$
C-H	$1.106 \pm 0.002\text{\AA}$
C-Cl	$1.762 \pm 0.002\text{\AA}$
β	$109.70 \pm 0.24^\circ$
θ	$19.47 \pm 1.06^\circ$
δ	$50.29 \pm 0.83^\circ$

STRUCTURE OF 4-CHLORONORTRICYCLENE



**THE STRUCTURES OF NORBORNANE AND 1,4-DICHLORONORBORNANE
AS DETERMINED BY ELECTRON DIFFRACTION**

J. F. Chiang, C. F. Wilcox, Jr. and S. H. Bauer

Department of Chemistry, Cornell University, Ithaca, New York 14850

ABSTRACT

The structures of norbornane and 1,4-dichloronorbornane in the vapor state as determined by electron diffraction, provide geometric parameters (i) for calculating strain and non-bonded interaction energies in a representative rigid bicyclic hydrocarbon, and (ii) for assessing the influence on the skeletal structure due to substitution of highly electronegative groups at the 1,4 positions. Sectorial diffraction photographs obtained at Cornell University and at the University of Oslo of the same samples gave scattered intensity which were in complete agreement both in magnitude and angular scale over the regions they overlapped. The strain energy for norbornane as calculated according to the scheme of Allinger were compared with the experimentally determined value.

DISTANCES IN NORBORNANE

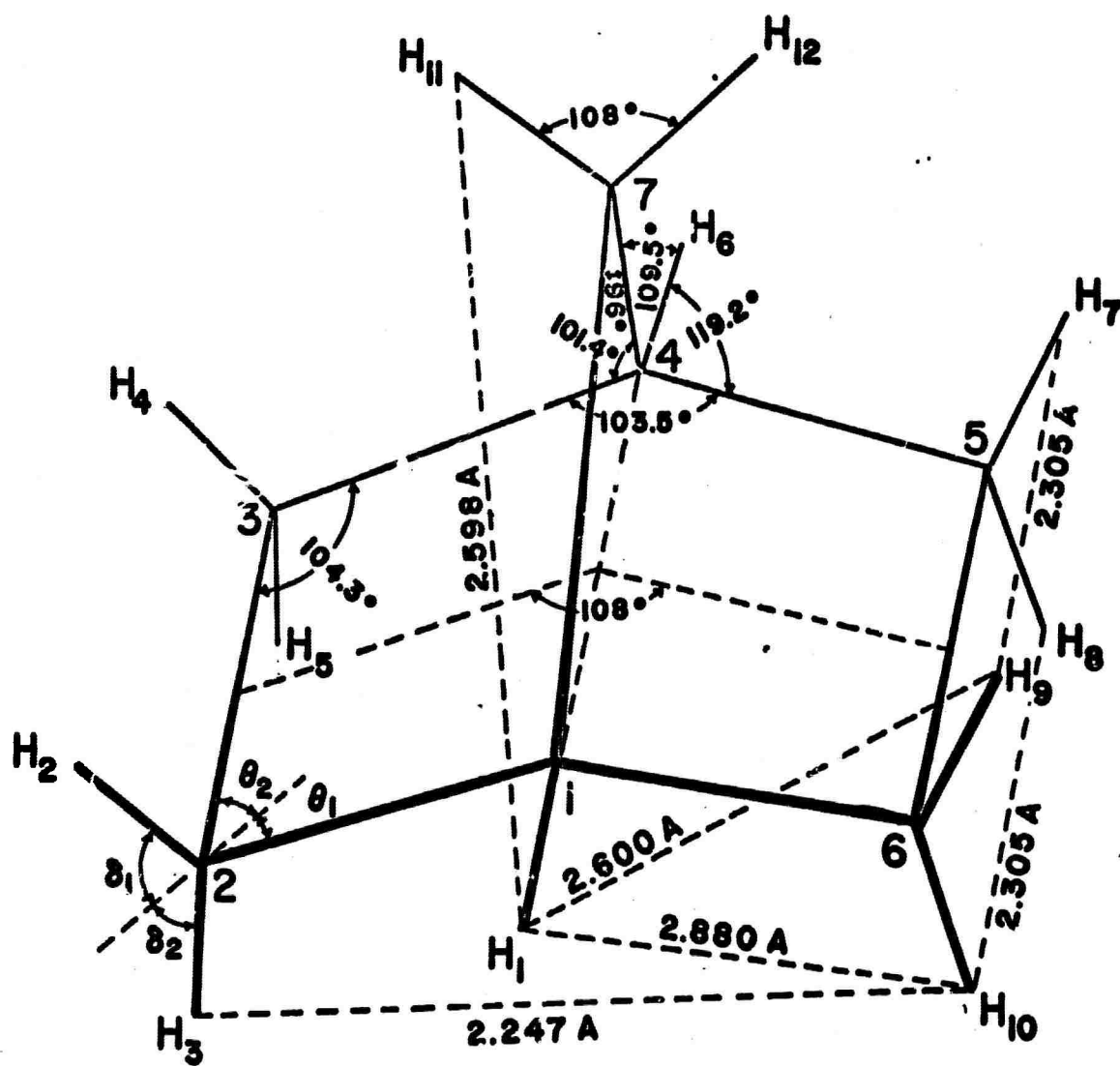
<u>Bonded</u>	<u>$r_{ij}(\text{\AA})$</u>	<u>$l_{ij}(\text{\AA})$</u>
$C_1-C_2, C_3-C_4, C_1-C_6, C_4-C_6$	1.556 ± 0.012	0.057 ± 0.004
C_2-C_3, C_5-C_6	1.551 ± 0.015	0.057 ± 0.004
C_1-C_7, C_4-C_7	1.559 ± 0.015	0.057 ± 0.004
$\langle C-H \rangle_{av}$	1.115 ± 0.015	0.080 ± 0.002
Bridge Angle	$96.0^\circ \pm 1.00^\circ$	
Flap Angle	$108.0^\circ \pm 1.50^\circ$	
$\angle H_{11}C_7H_{12}$	$108.0^\circ \pm 1.5^\circ$	
$\angle H_2C_2H_3$	$108.0^\circ \pm 1.0^\circ$	

(Assume $\theta_1/\theta_2 = 0.90$ and $\delta_1/\delta_2 = 1.00$)

Nonbonded Internuclear Distances

$C_1 \cdots C_4$	2.317 ± 0.020	0.093 ± 0.009
$C_1 \cdots C_3, C_2 \cdots C_4, C_1 \cdots C_5, C_4 \cdots C_6$	2.453 ± 0.030	0.083 ± 0.008
$C_2 \cdots C_6, C_3 \cdots C_5$	2.440 ± 0.033	0.083 ± 0.008
$C_2 \cdots C_7, C_3 \cdots C_7, C_5 \cdots C_7, C_6 \cdots C_7$	2.411 ± 0.027	0.085 ± 0.007
$C_2 \cdots C_5, C_3 \cdots C_6$	2.891 ± 0.036	0.086 ± 0.009

NORBORNANE



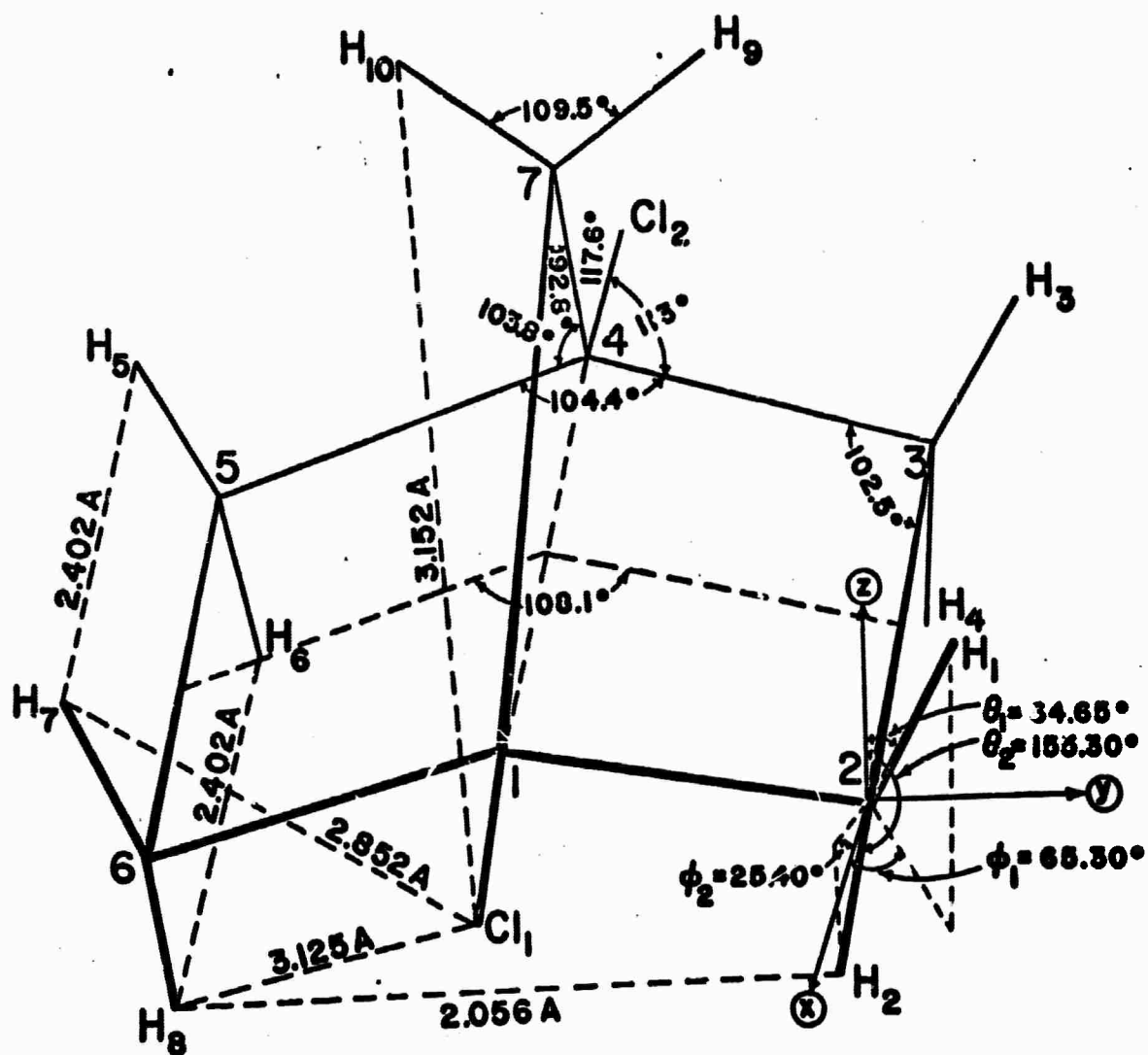
DISTANCES IN 1,4-DICHLORONORBORNANE

<u>Bonded</u>	<u>r_{ij} (Å)</u>	<u>d_{ij} (Å)</u>
$C_1-C_2, C_3-C_4, C_4-C_5, C_1-C_6$	1.556 ± 0.011	0.058 ± 0.003
C_2-C_3, C_5-C_6	1.553 ± 0.015	0.058 ± 0.003
C_1-C_7, C_4-C_7	1.539 ± 0.015	0.058 ± 0.003
$\langle C-H \rangle_{av}$	1.124 ± 0.021	0.079 ± 0.003
$C-Cl$	1.773 ± 0.008	0.056 ± 0.003
Bridge Angle	92.8 ± 1.0	
Flap Angle	$108.1 \pm 1.8^\circ$	
θ_1	$64.65 \pm 1.5^\circ$	
ϕ_1	$65.31 \pm 1.5^\circ$	
θ_2	$155.30 \pm 2.0^\circ$	
ϕ_2	$-25.40 \pm 1.8^\circ$	

Nonbonded Internuclear Distances

$C_1 \cdots C_4$	2.229 ± 0.009	0.130
$C_1 \cdots C_3, C_2 \cdots C_4, C_1 \cdots C_5, C_4 \cdots C_6$	2.426 ± 0.009	0.073
$C_2 \cdots C_6, C_3 \cdots C_5$	2.459 ± 0.010	0.077
$C_2 \cdots C_7, C_3 \cdots C_7, C_5 \cdots C_7, C_6 \cdots C_7$	2.435 ± 0.008	0.077
$C_2 \cdots C_5, C_3 \cdots C_6$	2.909 ± 0.011	0.110
$Cl_1 \cdots Cl_2$	$5.585 \pm 0.003A$	

1,4-DICHLORONORBORNANE



Contributions to the Strain Energy of Norbornane,
in kcal/mole, according to Allinger⁽¹⁵⁾

Bond Stretching	3.85
Angle Bending	7.47
Torsional	6.14*
Nonbonded Interactions	0.04
<hr/>	
Total (uncorrected for reference state)	17.50
Correction for reference compounds	- 0.38
<hr/>	
Total strain	17.12

* Of this total 1.45 kcal/mole arises from 1,4 non-bonded interactions.

STRUCTURES AND CONFORMATIONS OF THE CYCLOHEXADIENES

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ABSTRACT

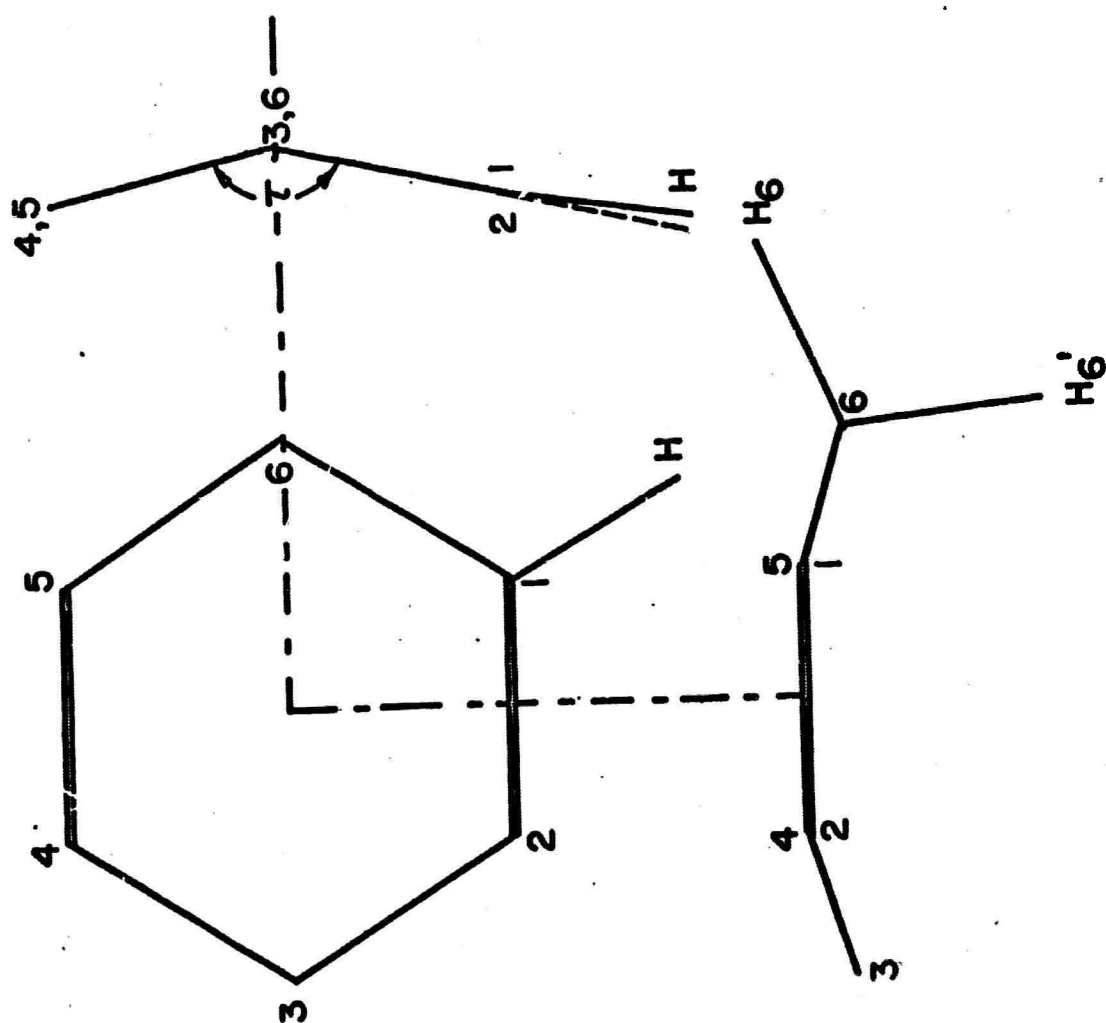
The structures of 1,3-cyclohexadiene and 1,4-cyclohexadiene in the gas phase were determined by electron diffraction. Interatomic distances and mean square amplitudes of vibration were evaluated. The structure found for the 1,3-isomer is in good agreement with the available microwave data. Of particular interest was the magnitude for the dihedral angle in the 1,4-isomer; it was found 159.3° , considerably larger than the value derived by minimizing angle strain and non-bonded hydrogen-hydrogen interactions. Various potentials for non-bonded H...H, C...H, and C...C interaction were used to deduce a larger dihedral angle, but the agreement with experiment is not as good as anticipated.

		B ₁	B ₂
1,3-C ₆ H ₈	25 kv	.066	0.0035
	75 kv	.123	0.0103
1,4-C ₆ H ₈	25 kv	.077	.0045
	75 kv	.135	.0118

Geometric Parameters for 1,4-C₆H₈

C ₁ C ₂	1.147 ± 0.004	
C ₁ C ₆	1.511 ± 0.004	
C ₁ H ₁	1.079 ± 0.010	
C ₆ H ₆	1.096 ± 0.012	
∠C ₂ C ₁ C ₆	122.7 ± 0.3°	
dihedral < τ	159.3 ± 0.7°	
∠C ₂ C ₁ H ₁	118.7° ± 1.2°	
∠C ₃ C ₆ H ₆	154.1° ± 4°	
∠H ₆ C ₆ H ₆ '	109.8° ± 4°	
ε	4.8° ± 3°	(out of plane, for C-H bonds on C=C)
∠C ₁ C ₆ C ₅	111.9°	(derived from above)

1,4 Cyclohexadiene

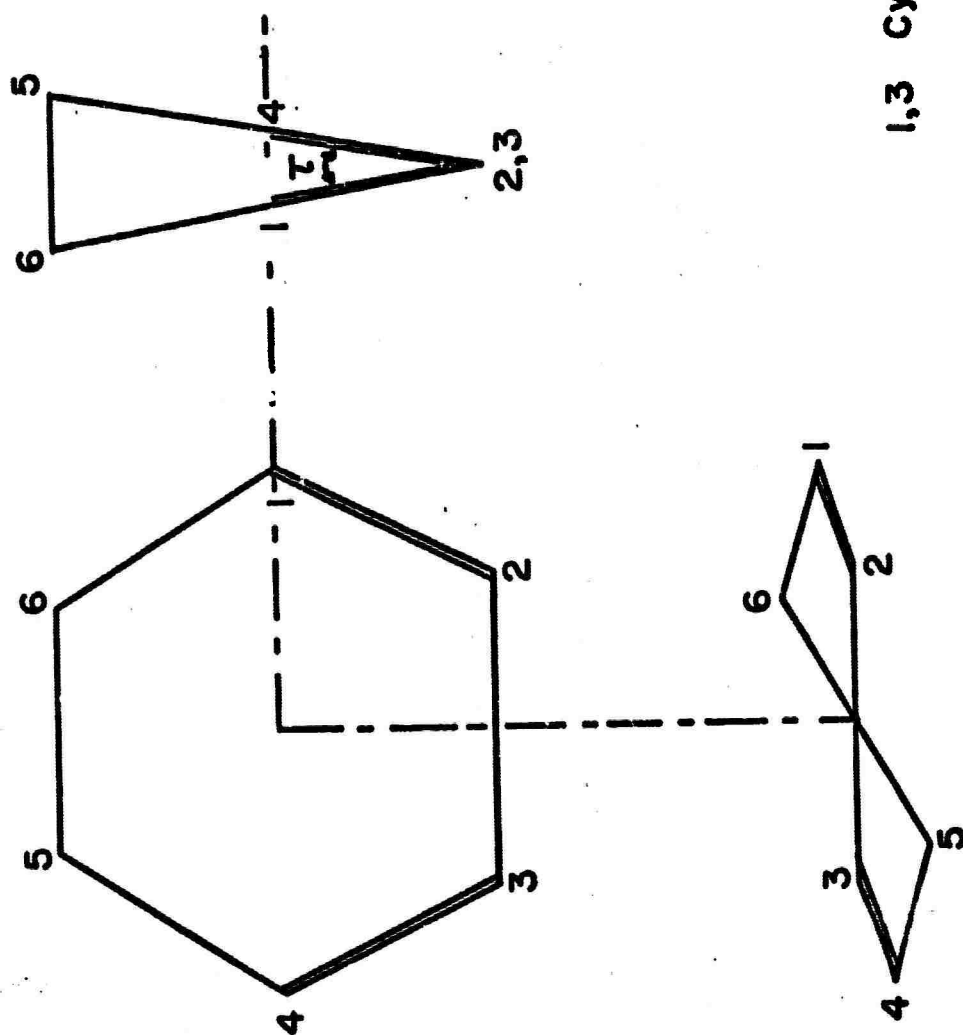


GEOMETRIC PARAMETERS FOR 1,3-C₆H₈

	<u>s.d.</u>	<u>S. S. Butler</u>
C ₂ C ₃	1.468 ± .014	1.47
C ₂ C ₁	1.350 ± .004	1.35
C ₁ C ₆	1.523 ± .016	1.50
C ₆ C ₅	1.534 ± .020	1.50
C ₂ H ₂	1.082 ± .010	1.086
C ₆ H ₆	1.096 ± .010	1.10
∠C ₃ C ₂ C ₁	120.13° ± 0.6°	120.16
∠C ₂ C ₁ C ₆	120.14° ± 0.5°	120.16
∠C ₁ C ₂ H ₂	122.0 ± 1.4	124°
∠C ₆ C ₁ H ₁	122.0 ± 1.4	122°
∠C ₅ C ₆ H ₆	106.8° ± 4.5°	103.5°
∠C ₁ C ₆ H ₆	109.3° ± 4.5°	109.5°
∠C ₅ C ₆ H ₆ '	111.1° ± 4.5°	109.5°
∠C ₁ C ₆ H ₆ '	105.0° ± 4.5°	109.5°
∠H ₆ C ₆ H ₆ **	114.1°	109.5°
∠C ₁ C ₆ C ₅ **	110.7°	110.5°
τ**, +	18.34°	17.5

** derived parameters

+ torsional angle through which one ethylene group is rotated relative to the other about the C₂C₃ bond.

1,3 Cyclohexadiene

THE STRUCTURE OF TRICYCLO[3, 3, 0, 0^{2, 6}]-OCTANE AS DETERMINED BY
ELECTRON DIFFRACTION

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ABSTRACT

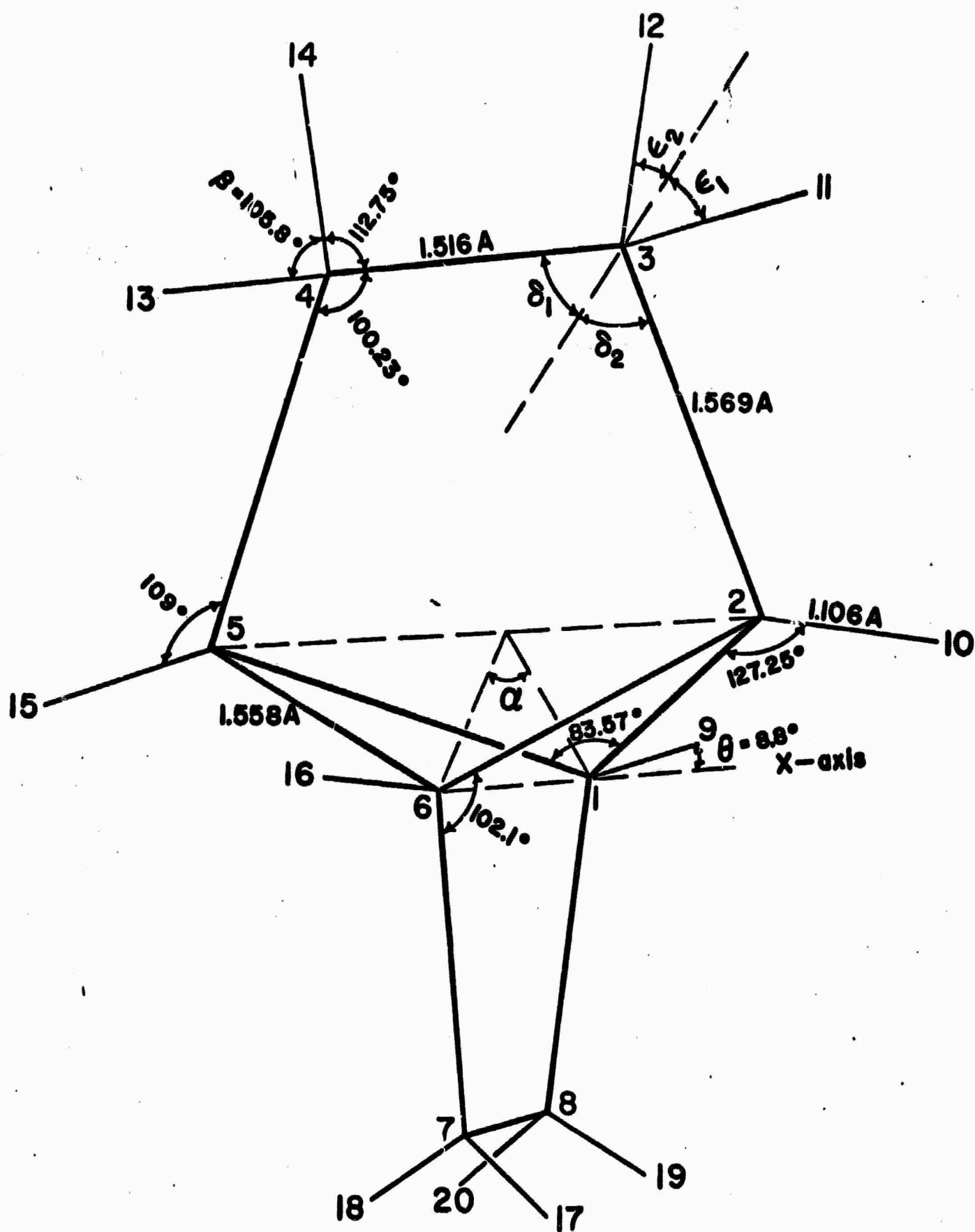
Tricyclo[3, 3, 0, 0^{2, 6}]octane was prepared from cis, cis-1,5-cyclo-octadiene by mercury sensitized photoisomerization. Sectorized diffraction photographs were taken with the sample of 0°C. With 70 kv electrons the recorded patterns covered the angular range $q = 0$ to 140 \AA^{-1} . The interatomic distances and bond angles in this highly strained, rigidly fused ring system were determined by resolution of the refined radial distribution curve, followed by a least squares fitting of the calculated molecular intensity pattern to that observed. Convergence was obtained for a structure with D_{2d} symmetry, in which the highly puckered four-member ring has $(C-C) = 1.558 \pm 0.003 \text{ \AA}$ with a dihedral angle of 127° . The sides of the five-member rings are $1.569 \pm 0.005 \text{ \AA}$ while their bases are $1.516 \pm 0.010 \text{ \AA}$; $(C-H)_{av} = 1.106 \pm 0.003 \text{ \AA}$. The root mean square amplitudes were found to be somewhat lower than for less rigidly bound hydrocarbons. Distortions of the four and five member rings in this octane are compared with rings in related molecules..

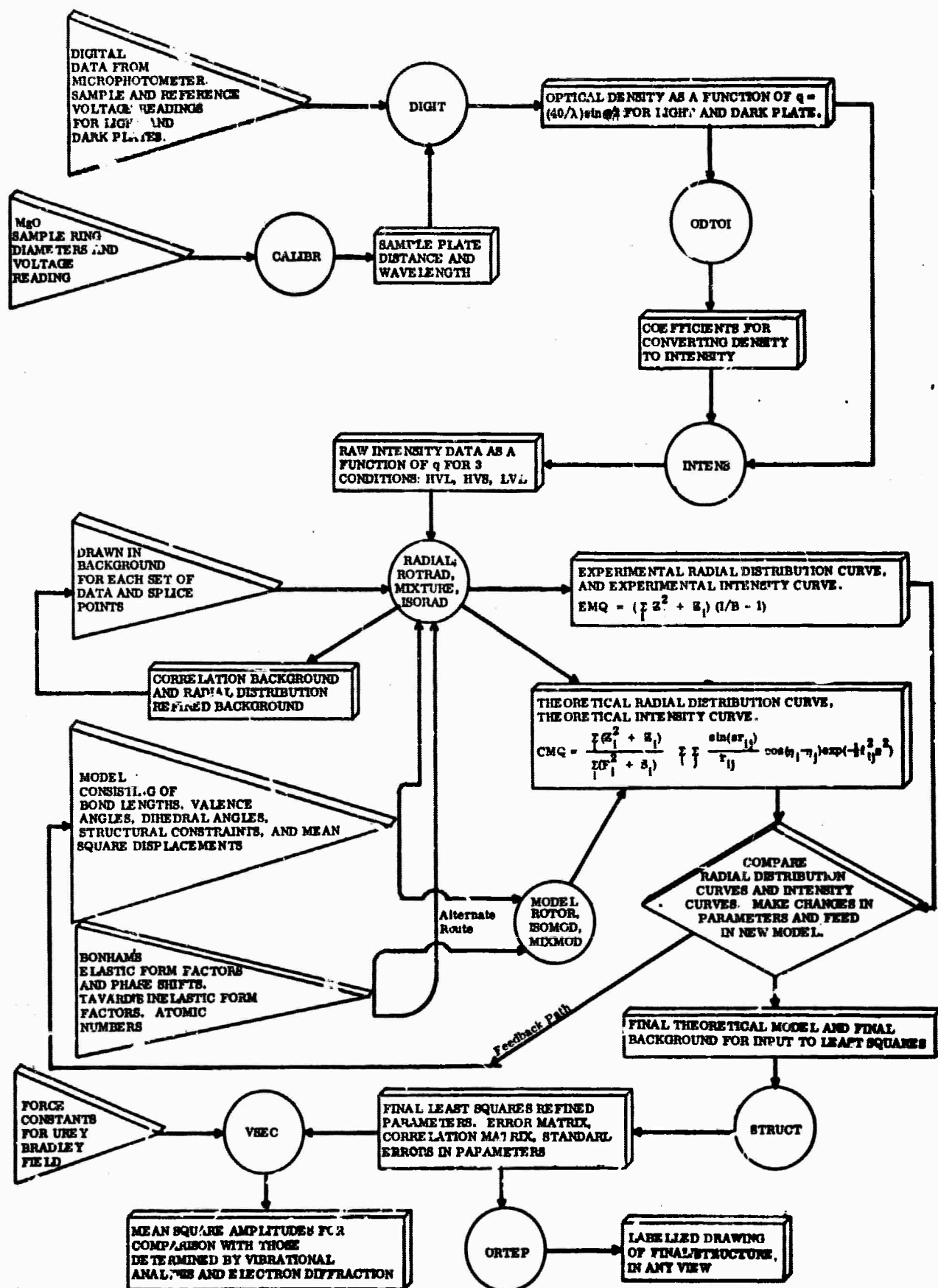
**STRUCTURAL PARAMETERS DERIVED BY LEAST SQUARES TREATMENT
OF DATA FOR TRICYCLO[3, 3, 0, 0^{2,6}]OCTANE**

	r_{ij}	ℓ_{ij}
C_1-C_2 [C_1-C_5 ; C_2-C_6 ; C_5-C_6]	$1.558 \pm 0.003A$	0.046 ± 0.0024
C_2-C_3 [C_4-C_5 ; C_1-C_6 ; C_6-C_7]	$1.569 \pm 0.0045A$	0.046 ± 0.0024
C_3-C_4 [C_7-C_8]	$1.516 \pm 0.010A$	0.046 ± 0.0024
$\langle C-H \rangle_{av}$	$1.106 \pm 0.003A$	0.082 ± 0.003
α	$126.7 \pm 0.3^\circ$	
β	$105.8 \pm 1.8^\circ$	
θ	$8.8 \pm 1.0^\circ$	

Calculated Nonbonded Distances (C...C)

$C_1 \dots C_3, C_1 \dots C_4, C_3 \dots C_6, C_4 \dots C_6$	2.433 ± 0.0027	0.0757 ± 0.0015
$C_2 \dots C_7, C_2 \dots C_8, C_5 \dots C_7, C_5 \dots C_8$		
$C_1 \dots C_7, C_6 \dots C_8, C_2 \dots C_4, C_3 \dots C_5$	2.369 ± 0.026	0.0715 ± 0.0030
$C_3 \dots C_7, C_3 \dots C_8, C_4 \dots C_7, C_4 \dots C_8$	3.765 ± 0.030	0.0715 ± 0.0030
$C_1 \dots C_6, C_2 \dots C_5$	2.077 ± 0.020	0.0593 ± 0.0036





DESCRIPTION OF PROGRAMS USED IN ELECTRON DIFFRACTION DATA REDUCTION

CALIBR - Voltage reading and the MgO ring radii are used as input. The program calculates a trial wavelength and sample-plate distance. The program then refines these parameters by the method of steepest descents.

DIGIT - Input consists of digitized data from microphotometer, the wavelength and sample-plate distance from CALIBR. DIGIT locates the center of the diffraction pattern and then interpolates densities to calculate the optical density at integral values of $q = 40/\lambda \sin \theta / 2$

ODTOI - Input is a series of equally spaced points on the curve DL vs DD [DD is the optical density of a dark plate and DL the optical density of a light plate.] The program then determines, by least squares, the power series coefficients of the curve

INTENS - Input is the optical density as a function of q from DIGIT plus the coefficients of the power for DL vs DD from ODTOI. Using these, the program calculates the scattering intensity vs density for the dark plate. Output is intensity vs q

RADIAL - Input consists of the intensity as a function of q , and a normally drawn-in trial background. The parameters (bond lengths, valence angles, etc.) for a trial model are also inserted into the program. Additional input are the mean square displacements and the form factors. For this trial model an $R(i, j)$ matrix is calculated, which in turn is used to calculate the molecular intensity curve $M(q)$, the nuclear intensity curve $MO(q)$, and the difference which is the electronic contribution to the scattering intensity $N(q)$. At the same time the experimental intensity curve is calculated from the equation $EM(q) = \sum_i (Z_i^2 + Z_i) [I(q)/B(q) - 1]$, where Z is the atomic number, $I(q)$ the intensity, and $B(q)$ the background.

In the next step the correlation background is calculated from the equation $CBAC(q) = I(q) / [(M(q) / \sum_i (Z_i^2 + Z_i) + 1)]$. This is the background which would be

obtained were the input model entirely correct and there were no extraneous scattering. It is useful for finding the best experimental background.

The radial distribution curve is then calculated. The RES factor (a scale factor defined as the ratio of the theoretical intensity to the experimental intensity) is calculated for the LVL (or HVL) data by integration of the theoretical intensity, integration of the experimental intensity, and taking the ratio of the two. The RES factors for HVL, and HVS data are then found relative to the LVL RES factor by comparing data at the splice points. Then the experimental nuclear scattering is computed by subtracting the theoretical electronic scattering from the experimental molecular scattering. Since the data do not extend to $q = 0$, the theoretical nuclear scattering is then spliced-in up to q_{min} for the LVL Data. This curve is then Fourier Inverted. At the same time the theoretical nuclear scattering is Fourier Inverted, providing a theoretical radial distribution curve for comparison.

Fluctuations about the base line in the known structureless regions of the radial distribution curve arise from errors in the first trial background and in the data. These fluctuations are then Fourier Inverted, thus providing corrections to the initial trial background.

ROTRAD - This program performs the same operations as program RADIAL, but was written for molecules which have internal rotations with a low barrier. The major difference is that instead of using one model, a weighted average of a sequence of models is computed. The weighting used depends on an assumed potential function for rotation.

MIXTURE - This program performs the same operations as program RADIAL but is written for a mixture of gases. The program averages over the models for the different components weighted according to their corresponding mole fractions.

MODEL - After the experimental intensity curve and experimental radial distribution curve have been found, this program is used as an alternate route to compute theoretical curves for comparison. In the same manner as in the program RADIAL.

Theoretical radial distributions are calculated by a superposition of Gaussian functions, whereas in RADIAL the function is derived by a Fourier Inversion.

ROTOR - This program bears the same relationship to MODEL as ROTRAD bears to RADIAL

ISOMOD - This program bears the same relationship to MODEL that ISORAD bears to RADIAL

MIXMOD - This program bears the same relationship to MODEL that MIXTURE bears to RADIAL

STRUCT - After several cycles of refinement of the background and model modifications with the above programs, the experimental and theoretical curves agree fairly well. At this point program STRUCT is used to optimize the data by least squares. The program uses the molecular intensity curve $EM(q)$ as its basis for fitting. This is a more reasonable choice than the radial distribution curve since it is closer to the raw experimental data. A conventional differential least squares technique is used. A correlation matrix and an error matrix are also calculated. Standard deviations for all the geometrical parameters and mean square amplitudes are calculated.

ORTEP - This is the Oak Ridge Thermal Ellipsoid Plotting program. Input consists of the cartesian coordinates of all the atoms, and many specifications as to how the picture should be drawn. Output is a labelled drawing of the molecule, drawn in perspective.

VSEC - This program, written by Shell Research, solves the normal coordinate-vibration problem. Input consists of cartesian coordinates of the atoms and constants for a Urey-Bradley force field. Output is a solution of the secular equation and the mean square displacements for all atom pairs. This program provides a useful correlation of our data with those doing research in infrared spectroscopy